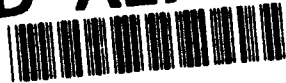


2

AD-A278 135



**Possible Effect of the Chlorine Oxide Dimer on
Transient Ozone Loss in Rocket Plumes**

15 March 1994

Prepared by

L. R. MARTIN
Mechanics and Materials Technology Center
Technology Operations

Prepared for

SPACE AND MISSILE SYSTEMS CENTER
AIR FORCE MATERIEL COMMAND
2430 E. El Segundo Boulevard
Los Angeles Air Force Base, CA 90245

DTIC
ELECT
S APR 18 1994
B

94-11484



1460

Development Group

94 4 15 054

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED

This report was submitted by The Aerospace Corporation, El Segundo, CA 90245-4691, under Contract No. F04701-93-C-0094 with the Space and Missile Systems Center, 2430 E. El Segundo Blvd., Los Angeles Air Force Base, CA 90245. It was reviewed and approved for The Aerospace Corporation by S. Feuerstein, Principal Director, Mechanics and Materials Technology Center.

This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

A handwritten signature in dark ink, appearing to read "John L. Edwards", is written over a horizontal line.

John Edwards
SMC/CEV

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 15 March 1994		3. REPORT TYPE AND DATES COVERED
4. TITLE AND SUBTITLE Possible Effect of the Chlorine Oxide Dimer on Transient Ozone Loss in Rocket Plumes			5. FUNDING NUMBERS F04701-93-C-0094	
6. AUTHOR(S) Martin, L. R.				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) The Aerospace Corporation Technology Operations El Segundo, CA 90245-4691			8. PERFORMING ORGANIZATION REPORT NUMBER TR-94(4231)-1	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Space and Missile Systems Center Air Force Materiel Command 2430 E. El Segundo Boulevard Los Angeles Air Force Base, CA 90245			10. SPONSORING/MONITORING AGENCY REPORT NUMBER SMC-TR-94-14	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Understanding transient, local ozone holes that may be produced by solid rocket boosters in the stratosphere puts special demands on models. One must consider the time scales as well as the rates for all of the pertinent chemical reactions involved in the destruction of ozone. In this report, we show that consideration of the existence of the chlorine oxide dimer, Cl ₂ O ₂ , and consideration of the necessary time scale for ozone loss are essential for prediction of a transient ozone hole. We argue that photolysis of this species is the major source of atomic chlorine in the plume at 20 km, and the ClO + O reaction is the major source at 30 km, although both processes play a role at the higher altitude. Inclusion of the chlorine oxide dimer ozone destruction cycle, which has not been considered in any of the full-scale models to date, predicts substantial ozone destruction on a scale of about 12-km diameter at 20-km altitude and the ClO cycle produces a 49-km-diameter hole at 30-km altitude. This analysis also suggests that the size of the hole at 20 km may be highly variable since it is sensitive to the variable ozone-to-methane ratio at that altitude.				
14. SUBJECT TERMS Ozone, Rocket launch, Stratospheric, Chlorine			15. NUMBER OF PAGES 16	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT	

Preface

I want to thank Paul Zittel, Norm Cohen and John Edwards for sharing information and for many useful and interesting conversations.

Accession For	
NTIS	<input checked="checked" type="checkbox"/>
DTIC	<input type="checkbox"/>
UL	<input type="checkbox"/>
JA	<input type="checkbox"/>
By	
Distribution	
Available to	
Dist	Special
A-1	

Contents

1. Introduction.....	1
2. Ozone Destruction Cycles.....	3
3. Estimate of Significance.....	5
4. Rocket Chlorine Loading	9
5. Final Considerations.....	11
5.1 Persistence of the Effect.....	11
5.2 Effect of Natural Methane and Hydrogen.....	11
5.3 Are Other Processes Rate Limiting?.....	12
5.4 Are Other Cycles Important?.....	12
References.....	15

Tables

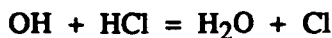
1. Concentrations of Pertinent Species, in Molecules/cc.....	5
2. Kinetic and Equilibrium Data	5
3. Summary of Back-Calculation of Required Chlorine Loading	9
4. Stratospheric Loading of HCl from Launches in Tons	9

1. Introduction

Solid rocket boosters release HCl and Cl atoms directly into the stratosphere. This release may produce "local" transient effects or global, long-term effects on the ozone layer. In this report, we consider the special situation created locally by such a launch. For the purposes of calculation, we will consider the time scale of interest to be about a day, or 10^5 seconds.

This zero-dimensional, back-of-the-envelope calculation is not intended as a substitute for a computer model. We are assuming an isothermal plume at the local stratospheric temperature, and we are neglecting most HO_x and NO_x reactions. Mass transfer problems are also not considered, so there is an implicit assumption of uniform mixing with the surrounding stratosphere out to the scale of 30 km within a day. Nevertheless, the calculations given here are a necessary, but not sufficient, condition for the significance of the reactions, and computer modelers ignore such reactions at risk.

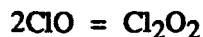
Work at The Aerospace Corporation and elsewhere has shown that afterburning in the rocket plume will convert a substantial fraction of the HCl to Cl_2 molecules, which, in turn, will photolyze to Cl atoms within a few minutes.¹ Conversion takes place because the afterburning produces high local concentrations of H and O atoms and OH radicals:



The chlorine atoms will react directly with ozone to cause local removal:



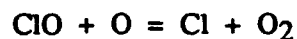
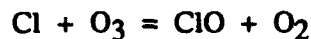
This is not a catalytic cycle, and the models to date for this process do not include the possible effects of further reactions on ozone loss. Because this reaction will greatly elevate the local concentration of ClO, it is important to explore the possibility of further reactions of this molecule. A likely reaction of interest is the formation of the chlorine oxide dimer:



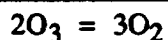
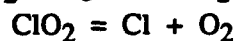
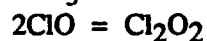
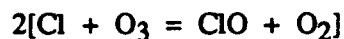
The chemistry of the chlorine oxide dimer has not been included in any of the plume models.²⁻⁵ The reason this may be important is that this molecule introduces a new ozone destruction cycle that does not require the presence of atomic oxygen in order to operate.

2. Ozone Destruction Cycles

The "normal" ozone destruction cycle [Cycle I] at mid-latitudes is:



The requirement for atomic oxygen means that this cycle is essentially inoperative at low altitudes—say 20 km. The chlorine oxide dimer cycle, which is responsible for the Antarctic ozone hole, does not require atomic oxygen and, therefore, is allowed to operate at low altitudes [Cycle II]:



This cycle takes place in the Antarctic because the low temperatures favor the formation of the dimer. As we will show below, the elevated local chlorine concentrations in a plume will also favor the formation of the dimer, and an enhancement of the ozone destruction is anticipated.

3. Estimate of Significance

To begin an estimate of significance, we will need to present some numbers. Table 1 gives a set of concentrations in the present-day stratosphere, i.e., with 3.5 ppb of chlorine. The two altitudes chosen are 20 km, which is the peak ozone density, and 30 km, which is close to the peak ozone mixing ratio. These numbers are taken from three sources.^{6,7,8} Given the variability with season, time of day, latitude, etc., the numbers are not meaningful to better than a factor of two.

Table 2 provides some necessary rate constants and equilibria computed at the two altitudes. We have chosen the U. S. Standard Atmosphere for the temperatures,⁷ and the rate constant for the Cl + O₃ reaction from Hampson's compilation:⁹

$$k_1 = 2.8 \times 10^{-11} e^{-257/T}$$

Table 1. Concentrations of Pertinent Species, in Molecules/cc

Species	20 km	30 km
Air	1.85×10^{18}	3.82×10^{17}
O ₃	5.0×10^{12}	2.5×10^{12}
CH ₄	3.0×10^{12}	2.1×10^{11}
HCl	1.1×10^9	5.0×10^8
ClNO ₃	3.7×10^8	5.0×10^8
ClO	2.8×10^7	1.5×10^8
O	1.5×10^6	6×10^7
OH	6×10^5	1.8×10^6
Cl	8×10^2	2.1×10^4

Table 2. Kinetic and Equilibrium Data

Altitude, km	20	30
Temperature, K	217	227
$k_1, \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	8.57×10^{-12}	9.03×10^{-12}
k_p , Photolysis Rate Constant of Cl ₂ O ₂ , s ⁻¹	1.3×10^{-3}	1.7×10^{-3}
K_1^* , cm ³ molecule ⁻¹	2.52×10^{-10}	4.48×10^{-11}

The photolysis rate for the chlorine oxide dimer has been calculated by integrating the photon flux model of Ackerman¹⁰ with cross sections from DeMore, et al.¹¹ The equilibrium constants were calculated from the expression of Cox and Hayman.¹²

$$K_p (\text{atm}^{-1}) = K_1^* (RT)^{-1}$$

$$= (e^{-144/R})(e^{+72,500/RT}) \quad (R \text{ in J mol}^{-1} \text{ K}^{-1})$$

$$K_1^* = [\text{Cl}_2\text{O}_2]/[\text{ClO}]^2 \quad (\text{cm}^3 \text{ molecule}^{-1})$$

Photolysis of the chlorine oxide dimer to provide chlorine atoms has been confirmed experimentally by Molina, et al.¹³

The natural turnover rate of ozone in the stratosphere at steady state is quite slow. This time is given by the ozone concentration divided by the odd oxygen loss rate,⁸ and is about 14 days at 30 km and 600 days at 20 km (turnover by chemical reaction only; mass transfer will be faster at this altitude). Thus, in order to create a local ozone depletion, it is not sufficient merely to compete with the natural turnover of ozone; it is necessary to remove ozone on a time scale of the physical and chemical dispersal of the rocket plume. Since we have chosen 10^5 s as the time scale of interest, it is necessary to find a process that will remove ozone on this time scale. Thus:

$$10^5 = [\text{O}_3]/\text{ozone loss rate}$$

We then back-calculate to get the amount of chlorine oxide loading required to do this. This is done in the following steps:

1. Calculate necessary ozone loss rate as shown above.
2. Calculate the chlorine atom concentration required to give this loss rate:

$$[\text{Cl}] = \text{ozone loss rate}/k_1[\text{O}_3]$$

3. Calculate the chlorine atom production rate required to get this steady-state concentration of chlorine atoms. This must come from photolysis of the chlorine oxide dimer, which ultimately yields two chlorine atoms per photolysis:

$$[\text{Cl}] = \text{production rate/loss rate} = 2k_p[\text{Cl}_2\text{O}_2]/k_1[\text{O}_3]$$

4. Step 3 gives the needed chlorine oxide dimer concentration. From this and the equilibrium constant, we can calculate the required chlorine oxide concentration:

$$[\text{ClO}] = \{[\text{Cl}_2\text{O}_2]/K_1^*\}^{1/2}$$

5. The sum of chlorine oxide and the dimer gives a required total chlorine concentration (for the short term). This and the rocket loading rate of active chlorine give an effective area within which this rate of ozone destruction takes place:

$$\text{Area in km}^2 = (\text{active chlorine loading in tons/km})/(\text{required chlorine in tons/km}^3)$$

From this, we can calculate an effective "hole" diameter due to the plume. A summary of the numbers in steps 1-4 for the two altitudes is shown in Table 3.

Table 3. Summary of Back-Calculation of Required Chlorine Loading

Altitude, km	20	30
Required Ozone Loss Rate, molecules $\text{cm}^{-3} \text{s}^{-1}$	5.0×10^7	2.5×10^7
Required [Cl], molecules cm^{-3}	1.17×10^6	1.11×10^6
Required Cl production rate, molecules $\text{cm}^{-3} \text{s}^{-1}$	1.00×10^8	2.6×10^7
Required $[\text{Cl}_2\text{O}_2]$, molecules cm^{-3}	1.93×10^{10}	7.8×10^9
Required [ClO], molecules cm^{-3}	8.73×10^9	1.32×10^{10}

4. Rocket Chlorine Loading

Table 4 gives the loading rates for both the Space Shuttle and the Titan IV as a function of altitude. This was calculated from the total loading rates of Brady, et al.,¹⁴ and the altitude profiles from an Aerodyne report.¹⁵ The percent active chlorine is the fraction of total chlorine present as Cl or Cl₂, calculated by Zittel.¹ From the mass of active chlorine, we may estimate that the effective plume diameter with an average concentration of ClO_x sufficiently high to deplete ozone locally by 63% (1/e level) in one day is 17 km in diameter at 20 km altitude and 29 km in diameter at 30 km altitude. The considerations given below reduce the estimated size at 20 km altitude to about 12 km, but will increase the size at 30 km altitude to about 49 km. This is substantially larger than the hole produced immediately by the Cl atoms released by afterburning in the plume.

Table 4. Stratospheric Loading of HCl from Launches in Tons

Altitude, km	Titan IV	% Active Chlorine (1)	Shuttle
15-20	10.2	21.2	22.0
20-25	9.8	35.8	17.2
25-30	9.0	65.7	13.9
30-35	8.4	65.7	11.3
35-40	6.8	75.7	9.0
40-45	2.9	75.7	4.0
45-50	1.0		1.5
Total in Stratosphere	48.1		78.9
Tons per Kilometer			
	@20 km	@ 30 km	
Titan IV	2.0	1.8	
Shuttle	3.9	3.0	

5. Final Considerations

5.1 Persistence of the Effect

The excess local ClO_x will gradually convert to HCl because of reactions of the Cl atoms with H -containing species, including CH_4 , H_2 , HNO_3 , HO_2 , and H_2O_2 . The time for this will be given by:

$$= (\text{characteristic time for Cl + RH reactions})[\text{ClO}_x]/[\text{Cl}]$$

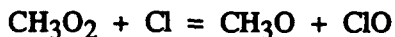
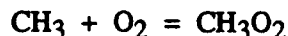
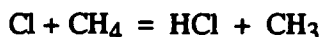
$$= (1/[\text{RH}]k_H)[\text{ClO}_x]/[\text{Cl}]$$

$$= 8.9 \text{ days @ 20 km, 16 days @ 30 km.}$$

Therefore, dissipation of the plume by mass transfer should take place faster than the decay of the chlorine oxide species.

5.2 Effect of Natural Methane and Hydrogen

The stratosphere at 20 km contains about 1.5 ppm of methane and 0.5 ppm of hydrogen, both from natural sources. At 30 km, these mixing ratios are reduced because of increasing loss of the methane and hydrogen through reactions with chlorine and OH . If the local ozone is completely removed by reaction with high concentrations of chlorine atoms, then these gases will scavenge chlorine also. Each methane molecule will remove at least one atom of chlorine, and each hydrogen molecule will remove two atoms of chlorine. Thus, at 20 km, the amount of chlorine removed by methane and hydrogen (total equivalent to 2.5 ppm) is roughly equal to the amount of ozone (2.7 ppm). This will reduce the amount of available ClO by a factor of roughly two, with a corresponding reduction in the hole size by the square root of two. This effect may be offset to an extent by the reaction sequence:



The third reaction above has never been studied, but it is thermodynamically allowed. By creating additional ClO , it can reduce the loss of active chlorine by up to half of the methane concentration (0.7 ppm).

The loss of active chlorine by reaction with the background methane and hydrogen leads to an additional consideration. The ratio of ozone to methane in the natural stratosphere is highly vari-

able,⁷ and, therefore, the "hole" size may be expected to be highly variable also. Thus, a single event may not be sufficient to characterize the typical effect of launches on the local ozone layer.

5.3 Are Other Processes Rate Limiting?

The characteristic time for formation of the chlorine oxide dimer from the monomer is given by the three-body rate constant for:

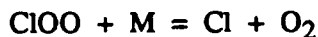


This has been given by DeMore, et al.^{11,16} as:

$$k_2 = 1.9 \times 10^{-32} (300/T)^{3.9} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \quad (\text{low pressure limit}).$$

Applying this rate constant to the situation in the plume gives a pseudo-first-order characteristic time of 170 s at 20 km and 1600 s at 30 km. This is faster than the characteristic time for photolysis at 20 km (700 s), so the formation of the dimer will not be rate limiting at this altitude. At 30 km, the photolysis time is about 600 s, so the rate of dimerization will limit the rate of ozone destruction at this altitude, and the effective hole size due to Cycle II will be about 60% of the size calculated above. However, as we will show below, ozone destruction from Cycle I will dominate the transient ozone loss at 30 km, so a large hole is still predicted (see below).

Lastly, the rate for the decomposition of the photolyzed chlorine radical

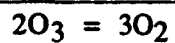
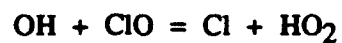
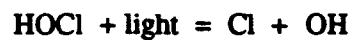
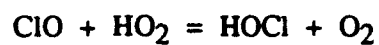


is very fast, with a lifetime of only 5 μs at 20 torr in laboratory experiments,¹³ so this step should not be rate limiting under any circumstances in the stratosphere.

5.4 Are Other Cycles Important?

It is interesting to consider the effect of the "normal" ozone destruction cycle (Cycle I) as local chlorine is elevated. We can go through the same kind of analysis as in Table 3 to estimate how much ClO is required to destroy ozone on the required time scale, via the $\text{ClO} + \text{O}$ reaction. Since atomic oxygen is not very abundant, about 850 ppb of ClO will be required at 20 km, and 26 ppb at 30 km. This means that a hole from this effect will be only about one-sixth as large as the hole due to Cycle II at 20 km, but at 30 km, Cycle I is more effective, and there should be about a 70% larger diameter hole (49-km diameter) than that caused by Cycle II. This effect, as before, will last as long as the excess ClO-to-HCl ratio lasts. Therefore, both ClO and its dimer will have to be considered. Heterogeneous chemistry can potentially change this picture by direct ozone destruction or possibly by the introduction of new reactions that convert ClO_x to Cl or Cl_2 .

In view of the elevated ClO concentrations, we also considered the possible impact of "Cycle III", which was originally proposed by Solomon, et al.:¹⁷



The photolytic lifetime of HOCl is about an hour at these altitudes. The slowest step in this cycle is the OH + ClO reaction, and about 1–2 ppm of ClO would be required to compete with Cycles I and II. Therefore, this does not appear to be an important cycle for transient ozone destruction.

References

1. P. F. Zittel, *Local Effects of Large, Solid Rocket Motors on Stratospheric Ozone*, ATR-92(9558)-2, The Aerospace Corporation (August 10, 1992).
2. M. J. Prather, et al., "The Space Shuttle's Impact on the Stratosphere," *J. Geophys. Res.* 95 583-98, 590 (1990).
3. I. E. Karol, et al., "Effect of Space Rocket Launches on Ozone," *Ann. Geophysicae* 10 810-814 (1992).
4. A. R. Douglass, et al., "Comparison of Model Results Transporting the Odd Nitrogen Family With Results Transporting Separate Odd Nitrogen Species," *J. Geophys. Res.* 94 9862-9872 (1989).
5. M. W. Ko, et al., "The Roles of Dynamical and Chemical Processes in Determining the Stratospheric Concentration of Ozone in One-Dimensional and Two-Dimensional Models," *J. Geophys. Res.* 94 9889-9896 (1989).
6. F. S. Rowland and M. J. Molina, "Chlorofluoromethanes in the Environment," *Rev. Geophys. and Space Phys.* 13 1- 35 (1975).
7. "The Natural Stratosphere of 1974," *CIAP Monograph 1*, DOT-TST-75-51, U. S. Department of Transportation , Washington, D. C., 22151 (September 1975).
8. M. B. McElroy and R. J. Salawitch, "Changing Composition of the Global Stratosphere," *Science* 243 763-770 (1989).
9. R. F. Hampson, *Chemical Kinetic and Photochemical Data Sheets for Atmospheric Reactions*, FAA-EE-80-17, U. S. Department of Transportation, Washington, D. C. 20591, April 1980.
10. M. Ackerman, "Ultraviolet Solar Radiation Related to Mesospheric Processes," in *Mesospheric Models and Related Experiments*, G. Fiocco, Ed., published by D. Reidel, Hingham, MA (1971).
11. W. B. DeMore, et al., *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*, Evaluation Number 10, JPL Publication 92, Jet Propulsion Laboratories, (20 August 1992).
12. R. A. Cox and G. D. Hayman, "The Stability and Photochemistry of Dimers of the ClO Radical and Implications for Antarctic Ozone Depletion," *Nature* 332 796-800 (1988).
13. M. J. Molina, et al., "Quantum Yield of Chlorine-Atom Formation in the Photodissociation of Chlorine Peroxide (ClOOCl) at 308 nm," *Chem. Phys. Lett.* 173 310-315 (1990).
14. B. B. Brady, et al., *Stratospheric Ozone-Depleting Chemicals Generated by Space Launches Worldwide*, TOR-93(3232)-3, The Aerospace Corporation (July 1993).

15. C. E. Kolb, et al., *Assessment of the Impact of Chemical Propulsion Exhaust Species on Stratospheric Ozone*, ARI-RR-787, Aerodyne Research Inc (1990).
16. S. P. Sander, et al., "Rate of Formation of the ClO Dimer in the Polar Stratosphere: Implications for Ozone Loss," *Science* 245 1095-1098 (1989).
17. S. Solomon, et al., *Nature* 321 755 (1986).

TECHNOLOGY OPERATIONS

The Aerospace Corporation functions as an "architect-engineer" for national security programs, specializing in advanced military space systems. The Corporation's Technology Operations supports the effective and timely development and operation of national security systems through scientific research and the application of advanced technology. Vital to the success of the Corporation is the technical staff's wide-ranging expertise and its ability to stay abreast of new technological developments and program support issues associated with rapidly evolving space systems. Contributing capabilities are provided by these individual Technology Centers:

Electronics Technology Center: Microelectronics, solid-state device physics, VLSI reliability, compound semiconductors, radiation hardening, data storage technologies, infrared detector devices and testing; electro-optics, quantum electronics, solid-state lasers, optical propagation and communications; cw and pulsed chemical laser development, optical resonators, beam control, atmospheric propagation, and laser effects and countermeasures; atomic frequency standards, applied laser spectroscopy, laser chemistry, laser optoelectronics, phase conjugation and coherent imaging, solar cell physics, battery electrochemistry, battery testing and evaluation.

Mechanics and Materials Technology Center: Evaluation and characterization of new materials: metals, alloys, ceramics, polymers and their composites, and new forms of carbon; development and analysis of thin films and deposition techniques; nondestructive evaluation, component failure analysis and reliability; fracture mechanics and stress corrosion; development and evaluation of hardened components; analysis and evaluation of materials at cryogenic and elevated temperatures; launch vehicle and reentry fluid mechanics, heat transfer and flight dynamics; chemical and electric propulsion; spacecraft structural mechanics, spacecraft survivability and vulnerability assessment; contamination, thermal and structural control; high temperature thermomechanics, gas kinetics and radiation; lubrication and surface phenomena.

Space and Environment Technology Center: Magnetospheric, auroral and cosmic ray physics, wave-particle interactions, magnetospheric plasma waves; atmospheric and ionospheric physics, density and composition of the upper atmosphere, remote sensing using atmospheric radiation; solar physics, infrared astronomy, infrared signature analysis; effects of solar activity, magnetic storms and nuclear explosions on the earth's atmosphere, ionosphere and magnetosphere; effects of electromagnetic and particulate radiations on space systems; space instrumentation; propellant chemistry, chemical dynamics, environmental chemistry, trace detection; atmospheric chemical reactions, atmospheric optics, light scattering, state-specific chemical reactions and radiative signatures of missile plumes, and sensor out-of-field-of-view rejection.